

Simulation and Experimental Research

Abstract: The usefulness of computer simulation in interpreting and extending experimental information is presented via a practical example taken from the area of chemical metallurgy.

Introduction

Within the last few years simulation has achieved the position of a new discipline in engineering science. Its growth and development has led, however, to the appearance of two seemingly opposite types of researchers: the "pure simulator" and the "pure experimenter." The former tends to believe that computers are superior to experimental research; the latter grudgingly accepts the computer as being a "gigantic slide rule" and refuses to look further.

We intend to show in this paper that simulation can be used as a research tool to enable the experimenter to improve his interpretation of experimental data and the organization of his research effort. Simulation and experimentation, when combined, can make a research project less time consuming and more efficient.

In Fig. 1 a general four-stage scheme of approach is presented. In the first stage the apparatus construction, testing, and modification is combined with the computer as an aid to the experimenter in evaluating preliminary equipment performance and arriving at the best possible apparatus design. In the second stage data provided by the working apparatus is processed by the computer and experimental conditions are logically set. At this stage the working apparatus-computer dialogue is still based on numerical data and preliminary calculations to eliminate unnecessary experimental conditions prior to establishing a mathematical model for the system. In the third stage a system model is developed on the basis of the logged and analyzed data. Not only can the experimenter expect a statistically more reliable model on account of the computer's ability to handle a large quantity of data, but he will also be able to consider the effect of numerous physical parameters. The distinction between the second and third

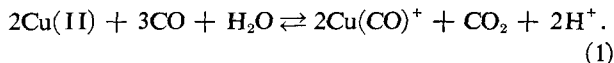
stages is not particularly sharp, as the experimenter may start out with some idea about the system model before experimentation. In the fourth stage the experimenter may predict new experimental data by simulation using the model devised in the previous stage and verify the simulated data by experiment. The simulation may also operate in parallel with experimentation and thereby function as a monitor by rendering immediately obvious any anomalies in the experimental data. The experimenter will now be in a position to decide if his study area and experimental technique need to be extended and, if so, at what stage the scheme should be retraced.

To illustrate the approach, an example is drawn from the area of chemical kinetics, where the traditional research philosophy is predominant.

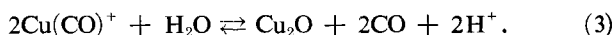
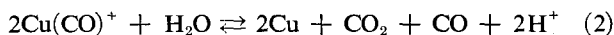
Example: Reduction of divalent copper by carbon monoxide

A number of metals have been successfully produced from aqueous solution when subjected to carbon monoxide. The severity of the conditions necessary for the reactions to proceed at reasonable rates may vary from atmospheric carbon monoxide pressure and room temperature to hundreds of atmospheres and possibly 250°C.

The reduction of divalent copper by carbon monoxide proceeds in two steps. In the first step copper(II) is reduced to copper(I), which follows the stoichiometry



In the second step copper(I) is either further reduced to metallic copper or hydrolyzed to cuprous oxide according to the reactions,



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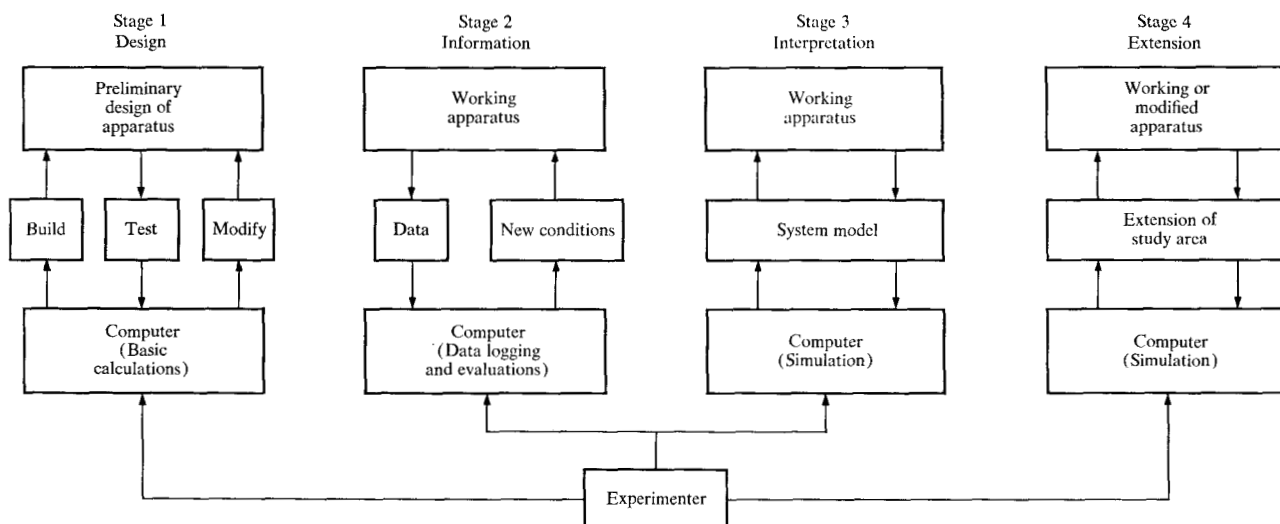


Figure 1 Scheme for combining experimental research and computer simulation.

The kinetics of the reaction given in Eq. (1) was first studied in acetate-buffered solutions by Peters and Byerley,¹ who formulated a two-term rate law to account for the observed kinetics:

$$-\frac{d[\text{Cu(II)}]^*}{dt} = k'_1 \frac{[\text{Cu(II)}][\text{Cu(I)}]}{[\text{H}^+]} + k'_2 \frac{[\text{Cu(II)}]^2}{[\text{H}^+]} P_{\text{CO}}, \quad (4)$$

where

$$k'_1 = 5.43 \times 10^{-6} \text{ sec}^{-1}.$$

$$k'_2 = 5.70 \times 10^{-9} \text{ sec}^{-1} \text{ atm}^{-1}$$

at 0.25M† NaOAc and 119.4°C.

Under the chemical conditions employed in the original investigation (0.1M Cu(II), 0.25M NaOAc, 0.50M HOAc, $P_{\text{CO}} = 68 \text{ atm}$. and temperature = 120°C represent average conditions) it was apparent that the second term of Eq. (4) accounted for less than 10% of the maximum observed reaction rate. This rather small contribution to the maximum rate not only made evaluation of the rate constant k'_2 subject to large errors (in general rate measurements on systems such as described here are rarely better than 5%), but frustrated any attempt to examine more thoroughly the chemical variables contained in the second term.

Earlier investigations carried out on similar chemical systems, particularly the silver(I)-carbon monoxide reac-

tion,² have resulted in reports of reaction paths that are independent of hydrogen ion concentration. If such a path existed in the reaction under discussion here, it would be accounted for in the second term of the rate expression, but its resolution was not possible under normal chemical conditions. Fortunately, the second term in the rate expression is pressure dependent, whereas the first term, which generally contributes 90% to the total maximum rate, is independent of pressure. This situation was exploited in a subsequent investigation³ by employing carbon monoxide pressures up to 1360 atm. Under this condition the rate due to the second term may account for as much as 40% of the total maximum rate. It was found that if the second term rate is plotted against the reciprocal of hydrogen ion concentration, the expected linear relationship was obtained along with a non-zero intercept. This implied that the second term may better be expressed by two terms, one of which is independent of hydrogen ion concentration. The rate law reported then has the form:

$$-\frac{d[\text{Cu(II)}]}{dt} = k_1 \frac{[\text{Cu(II)}][\text{Cu(I)}]}{[\text{H}^+]} + k_2 \frac{[\text{Cu(II)}]^2}{[\text{H}^+]} P_{\text{CO}} + k_3 [\text{Cu(II)}]^2 P_{\text{CO}}. \quad (5)$$

where

$$k_1 = 4.24 \times 10^{-6} \text{ sec}^{-1}$$

$$k_2 = 1.40 \times 10^{-9} \text{ sec}^{-1} \text{ atm}^{-1}$$

$$k_3 = 1.15 \times 10^{-4} \text{ sec}^{-1} \text{ M}^{-1} \text{ atm}^{-1}$$

at 0.25 M NaOAc and 119.4°C.

* Squared brackets denote concentration in moles per litre.
† M denotes moles per litre.

CONTINUOUS SYSTEM MODELING PROGRAM
A DIGITAL ANALOG SIMULATOR PROGRAM FOR THE IBM 1130

INSTRUCTIONAL COMMENTS MAY BE SUPPRESSED AT ANY TIME BY TURNING ON SWITCH 10
TURN ON SWITCH 1 TO ENTER OR MODIFY CONFIGURATION STATEMENTS VIA THE KEYBOARD
TURN ON SWITCH 2 TO ENTER OR MODIFY INITIAL CONDITIONS OR ELEMENT PARAMETERS VIA THE KEYBOARD
TURN ON SWITCH 3 TO ENTER OR MODIFY FUNCTION GENERATOR INTERCEPTS VIA THE KEYBOARD

OUTPUT NAME	BLOCK	TYPE	INPUT 1	INPUT 2	INPUT 3
DA / DT	3	G	1	0	0
BETA	12	K	10	0	0
(CO)	4	+	-9	0	0
P(CO)	5	F	3	11	0
	2	X	4	0	0
GAMMA	6	G	5	1	0
	7	+	6	12	0
	8	X	2	7	0
ALPHA	9	G	1	0	0
	11	K	0	0	0

IC/PAR NAME	BLOCK	IC/PAR1	PAR2	PAR3
BETA	12	-13.8000	0.0000	0.0000
ALPHA	9	0.1320	0.0000	0.0000
	1	0.0096	0.0000	0.0000
GAMMA	6	0.0114	0.0000	0.0000
	3	1.5000	0.0000	0.0000
	5	0.1410	0.0100	0.0000

5	13.4100	38.5000	63.5000	86.0000
	112.0000	141.0000	173.0000	204.0000
	238.0000	273.0000	318.0000	

[0.05] INTEGRATION INTERVAL
[100.] TOTAL TIME
[1] BLOCK FOR Y-AXIS [] MINIMUM VALUE [0.01] MAXIMUM VALUE
[] BLOCK FOR X-AXIS [] MINIMUM VALUE [] MAXIMUM VALUE

PREPARE PLOTTER AND PRESS START
SET PEN ABOUT ONE INCH FROM RIGHT MARGIN

TIME	OUTPUT(1)	OUTPUT(4)	OUTPUT(5)	OUTPUT(6)	OUTPUT(10)
0.000	0.0096	0.0404	70.7996	0.8120	-0.0000
20.000	0.0056	0.0345	60.2974	0.6916	-0.0003
40.000	0.0008	0.0273	46.5495	0.5339	-0.0001
60.000	0.0000	0.0261	44.3172	0.5083	-0.0000
80.000	0.0000	0.0260	44.1432	0.5063	-0.0000
100.000	0.0000	0.0260	44.1307	0.5061	-0.0000

AFTER SELECTING DESIRED OPTION PRESS START

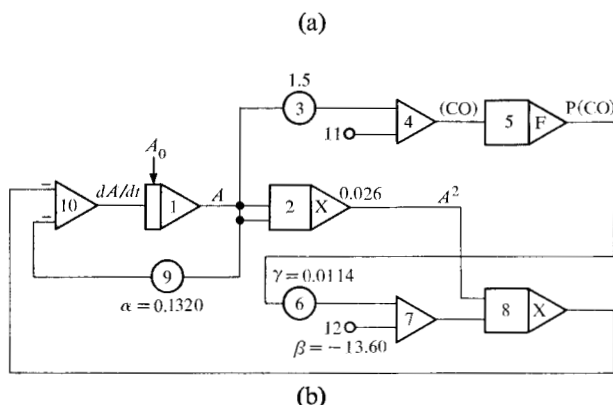


Figure 2 (a) Simulation via IBM 1130 CSMP of copper(II) reduction, (b) Block-oriented (analog computer) computer flow chart for the solution of Eq. (5). The rate equation is rewritten as $-dA/dt = \alpha A + A^2[\gamma P_{CO} + \beta]$, where $A \equiv \text{Cu(II)}$. The numerical values of the constants are calculated for experiment "b" (see Fig. 3).

This experimental rate law was used as the guide in postulating a reaction mechanism. The postulated mechanism must of course take into account the stoichiometry of Eq. (1) and the functional relationships of Eq. (5) besides incorporating chemically significant species. The postulated mechanism, as well as the kinetic analysis for resolving the various contributions to the total maximum observed rate, are given in reference 3.

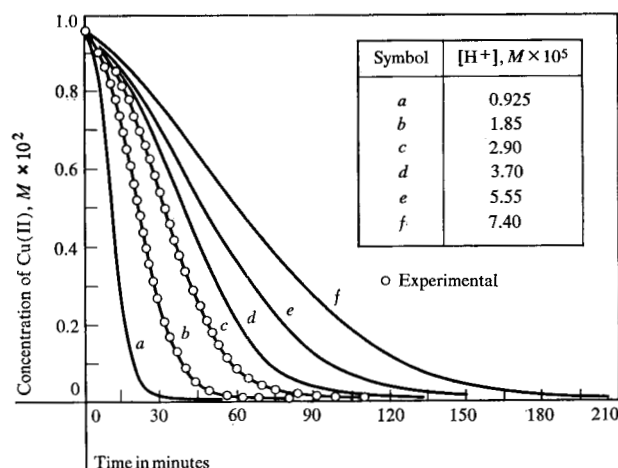


Figure 3 The variation of copper(II) concentration with time at various hydrogen ion concentrations; 0.25M NaOAc; $P_{CO} = 68$ atm; temperature = 119.4°C.

Simulation

In Fig. 2 simulation via the IBM 1130 Continuous System Modeling Program⁴ (CSMP) is shown for the experimentally studied case of 0.0096 M copper(II) and 0.035 M carbon monoxide initial concentrations. The first four lines are automatically typed in order to remind the programmer about basic switch manipulations. The Configuration Specification, Initial Conditions and Parameters and Function Generator Specifications sections are identical to those of the PACTOLUS digital simulator⁵ except for the Output Name and IC/PAR Name columns which facilitate block identification throughout the program. Below the timing specification entries there follow plotting specifications. Finally, the output of five blocks logically chosen are tabulated upon execution at 20-minute intervals. The last line is a reminder to specify further action, i.e., to change parameters, timing specifications, to plot, etc. . . . or to terminate execution. The function generator entry points are ten equidistant values of the carbon monoxide partial pressure/concentration of dissolved carbon monoxide data pairs scaled as

$$X_{sc} = \frac{100}{X_{\max} - X_{\min}} (X - X_{\min}). \quad (6)$$

In Fig. 3 the variation of copper(II) concentration with time is shown for a number of hydrogen ion concentrations. The open points on curves b and c are experimental values taken from the results of the original investigation. No particular significance should be attached to the chemical conditions chosen in the simulation as shown in Fig. 3. This figure is nothing more than a comparison of experimental and simulated data using a set of chemical variables that generate a typical family of rate curves.

Discussion

Complete development of the rate expression required many experiments, some under rather extreme conditions. The question now arises as to whether process simulation incorporated with experimentation would provide for a more efficient kinetic analysis of the system. It is apparent that once Eq. (4) has been tentatively established using a minimum amount of experimental data, it is a rather simple matter to predict via simulation the rate of reduction of copper(II) at any time for a wide range of chemical conditions, especially extreme conditions where experimentation is inconvenient, e.g., high pressure or high temperature. Thus, simulated data would not only provide a check for the experimental data, but extend the data into difficult experimental regions.

The existence of the third term may be predicted by simulation. As noted previously the only means of examining the second term with any degree of accuracy was under the condition of high carbon monoxide pressure. As long as the relationship between rate of reduction of copper(II) and carbon monoxide pressure has been established at modest pressures the process simulation can provide high pressure information which would resemble that depicted in Fig. 3, except quite different chemical conditions would be imposed. These data, unlike many cases where simulation results are relegated to the role of verification, can detect without experimentation the contribution to the total rate of a hydrogen ion-independent reaction. It is obvious that the simulation analysis, which may lead to a more complete description of the reaction kinetics, is a direct application of the last two stages of our proposed scheme. Once the system model

has been developed, no matter how crude the form, the computer simulation may provide the fine structure of the model or at least chart the path for extension of the study area.

Summary

Much research effort is centered on the extension of existing data in order that many models and theories may be more widely applicable. In so doing, the researcher must frequently employ extreme experimental conditions which at least impair the efficiency of the research and certainly the accuracy of the data. A judicious combination of experiments and simulation may not only monitor the experimental technique but may also aid in the interpretation of meager data and the design of future experiments.

Acknowledgment

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References

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